Accurate Mg/Ca, Sr/Ca, and Ba/Ca ratio measurements in carbonates by SIMS and NanoSIMS and an assessment of heterogeneity in common calcium carbonate standards


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ABSTRACT

As archives of past climate variability, the micron and sub-micron scales of element:calcium (Me/Ca) variability in both biogenic and inorganic carbonates contain important geochemical information. Ideally working at smaller and smaller scales leads to higher temporal resolution of past changes, but more often it has revealed the strong overprint of other processes on the climate signal. Therefore, the role of SIMS and NanoSIMS techniques in studying paleoenvironmental proxies continues to increase. We evaluate the accuracy and precision of the CAMECA ims 7F-GEO and NanoSIMS-50L ion probes for measurements of Sr/Ca, Mg/Ca, and Ba/Ca ratios in carbonate minerals. Nine carbonate reference materials were examined for their 88Sr/42Ca, 24Mg/42Ca, and 138Ba/42Ca ratios by a primary O beam with spot sizes of 20–40 μm (SIMS) and 0.8–2 μm (NanoSIMS). To assess accuracy, seven of these standards were analyzed for Sr/Ca and Mg/Ca with ID-ICP-MS. Variability in the elemental ratios arising from drift and changes in the tuning of the ims 7F-GEO over a nine month period is smaller than the chemical heterogeneity of the most frequently analyzed standards (OKA and Blue-CC). Across a whole crystal, Blue-CC is more homogeneous (1σ of 2.39% and 1.60% for Sr/Ca and Mg/Ca respectively) than OKA, but in the bulk matrix of OKA there is even less variability (1σ of 0.85% and 0.83% respectively). We find that carbonate samples can be accurately normalized to carbonate standards with significantly different absolute Me/Ca ratios. NanoSIMS intensity ratios follow counting statistics better than ±1% (2σ) at any one spot, but conversion to Me/Ca ratios increases the uncertainty. Two factors give rise to this limitation. First, the spatial heterogeneity of nominally homogeneous standards can lead to accuracy offsets that are as large as the ranges quoted above. Second, the NanoSIMS generates higher instrumental mass fractionation relative to SIMS. The combination of three different analytical techniques demonstrates that Blue-CC and homogeneous calcite zones in OKA are promising reference materials for precise analyzers. Accuracy is crucially dependent on making independent measurements on exactly the same crystal of standard used in the SIMS and NanoSIMS machines.

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1. Introduction

Secondary ion mass spectrometry (SIMS) has emerged as an important technique for characterizing the chemistry of carbonate minerals (Mason, 1987; Ricupi et al., 1994; Savard et al., 1995; Allison, 1996; Hart and Cohen, 1996; Denniston et al., 1997; Cohen et al., 2001; Finch et al., 2001; Heikoop et al., 2002; Meibom et al., 2004; Sano et al., 2005; Shirai et al., 2005; Weber et al., 2005; Cohen et al., 2006; Gaetani and Cohen, 2006; Kunioka et al., 2006; Meibom et al., 2006; Allison et al., 2007; Reynaud et al., 2007; Stolarski et al., 2007; Stoll et al., 2007; Allison and Austin, 2008; Meibom et al., 2008; Shirai et al., 2008; Cohen et al., 2009; Holcomb et al., 2009; Kasemann et al., 2009; Rollion-Bard et al., 2009; Rollion-Bard and Erez, 2010; Gabitov et al., 2011). This trend is motivated by the ability of SIMS to constrain both major and trace element abundances as well as isotope ratios at spatial scales of 20–30 μm (for most conventional instruments) to as small as 1 μm (for the NanoSIMS; or, in some cases, less; Badro et al., 2007; Meibom et al., 2008). Thus, ion probes are capable of measuring a range of analytes similar to laser ablation ICP-MS, but with a spatial resolution similar to the electron probe or secondary electron microscopy. And, as for all in situ methods, SIMS avoids the sample handling and potential contamination required for most wet chemical analysis techniques. Several reviews of relevant instruments and techniques describe these general strengths of SIMS for geoscience applications (Werner, 1978; Shimizu and Hart, 1982; Fayek, 2009, etc.).

One complication of SIMS analyses is that instrumental fractionations (i.e., differences between detected ion intensity ratios and corresponding abundance ratios of those elements or isotopes in the sample) are functions of the composition, structure and orientation of the sample. For example, Steele et al. (1981) showed that detected intensity ratios of Mg²⁺/Si⁴⁺ and Fe²⁺/Si⁴⁺ varied non-linearly with changing Mg/(Mg + Fe) in olivine and low-Ca pyroxene. These analytical artifacts...
arise from differential sputtering yields, differences in probabilities of ionization, and fractionations associated with ion optics and detector efficiencies. The term ‘matrix effects’ refers to the dependence of these analytical artifacts on the chemical and physical properties of the sample. While the family of processes governing matrix effects is recognized (Slodzian et al., 1980), it is generally unclear why a specific instrumental fractionation is observed for a specific material and instrument tuning condition. Therefore, the accuracy of SIMS measurements depends upon empirical standardization schemes in which it is assumed that the instrumental fractionation for an unknown sample is equal to that in a standard that is closely similar in chemistry and structure (and perhaps orientation) to the sample, analyzed under the same instrumental conditions as the unknown.

Standardization schemes for SIMS analyses are well established for a variety of analytes in a variety of targets, but the growing importance of this technique for the study of carbonates has raised two related problems that have not been satisfactorily resolved: (1) Natural carbonates are chemically and structurally complex, meaning a variety of standards are needed. And, natural carbonates are frequently heterogeneous, meaning many potential standards are actually ill suited to in-situ analyses (we will show here that one of the most common carbonate standards currently in use for trace element analyses is highly heterogeneous). It is not clear that we yet have a suitable set of interlaboratory standards. And, (2) many natural carbonates are compositionally zoned over very short length scales (~a few microns or less), meaning the NanoSIMS is the only class of ion probes suitable for consistently resolving zonation. But the NanoSIMS differs markedly in its ion optics from most other SIMS (e.g., its short distance between sample and extraction lens means ions are collected from a wider range of emission angles — i.e., the NanoSIMS actually analyzes populations of ions different from those collected on a conventional instrument). Very little data have been presented demonstrating the limits of accuracy and precision of NanoSIMS measurements of carbonates, or any distinctive behaviors it might exhibit with respect to matrix effects or instrumental fractionations generally.

This paper addresses these problems for SIMS and NanoSIMS measurements of Sr/Ca, Mg/Ca, and Ba/Ca ratios in natural carbonates. In particular, we examine the contributions to analytical uncertainties in such measurements arising from instrumental causes vs. those that arise from heterogeneity of several widely used carbonate standards.

We compare and contrast the performance of the ims 7F-GEO (a relatively conventional SIMS) and NanoSIMS-50L machines on a common set of standards and ratios (to the best of our knowledge, this is the first detailed comparison of the analytical capabilities of these two instruments for any substantial set of well-characterized materials). Finally, we also document the heterogeneity of each standard using a nested approach that lets us use measurements at a relatively coarse scale to calibrate the accuracy of groups of finer-scale in situ analyses. These data offer the first detailed documentation of the properties of a set of standards suitable for SIMS analysis of trace elements in carbonates, and demonstrates the limitations and controls of analytical accuracy and precision for such measurements with the NanoSIMS ion probe — the highest-resolution instrument available for in situ trace element analysis.

2. Methods

2.1. Standards analyzed

We analyzed Mg/Ca, Sr/Ca, and Ba/Ca ratios in nine natural calcites and aragonites: OKA, Blue-CC, AG-1, NBS-19, 135-CC, LAS-20, RPI-CC, HUJ-AR, and UCI-CC by measuring $^{42}\text{Ca}^+$, $^{44}\text{Ca}^+$, $^{88}\text{Sr}$, and $^{138}\text{Ba}$. Eight of these were analyzed by Isotope Dilution ICP-MS at Caltech for Sr/Ca and Mg/Ca, while AG-1 was analyzed for the same ratios at WHOI using a Thermo Scientific Element-II ICP-MS. OKA, Blue-CC, NBS-19, and LAS-20 are commonly used to standardize SIMS analyses of trace and minor elements in foraminifera, corals, or loculi calcites (Denniston et al., 1997; Cohen et al., 2001; Heikoop et al., 2002; Bice et al., 2005; Bond et al., 2005; Sano et al., 2005; Allison et al., 2007). 135-CC calcite is used as an electron microprobe standard at UC-Berkeley (http://epmalab.uoregon.edu/UCB_EPMA/standards.htm#calcite). RPI-CC has been used previously to standardize analyses of Sr and Pb in calcite (Cherniak, 1997). Each Me/Ca ratio (where Me stands for any metal other than Ca) spans over two orders of magnitude between all of the standards. Further details about each standard are presented in Appendix 1.

2.2. Inductively coupled mass spectrometry (ICP-MS)

Powders prepared from all nine carbonate standards were measured by ICP-MS at Caltech to provide an accurate reference frame for the SIMS and NanoSIMS measurements of Me/Ca ratios. Mg/Ca and Sr/Ca were measured using an improved version of the isotope-dilution method described in Fernandez et al. (2010) by adapting the method for a Neptune multi-collector ICP-MS (ThermoFinnigan). The external precision of the method was assessed by the regular analysis of a dissolved deep-sea coral consistency standard with a Sr/Ca ratio of 10.26 nmol/mol and a Mg/Ca ratio of 3.062 nmol/mol. For the two analytical sessions used in this study, the reproducibility of 8 consistency standards was 0.4‰ for Sr/Ca and 5‰ for Mg/Ca (2 standard deviations, relative error). This external error is a somewhat better than the long-term reproducibility of 98 consistency standard measurements over the last four years, which is 1‰ for Sr/Ca and 12‰ for Mg/Ca. Even using the more conservative long term reproducibility as an error estimate, analytical uncertainty is much smaller than most of the signals discussed in this paper. The external precision for Sr/Ca using our improved method is similar to more time consuming ID-TIMS methods (Beck et al., 1992; Devilliers et al., 1995) with an additional advantage that we can simultaneously measure Mg/Ca ratios with high precision. The ultimate accuracy of this method is set by our spike calibration as described in Fernandez et al. (2010).

2.3. SIMS

Before analysis in the Caltech Microanalysis Center with Cameca ims 7F-Geo, all samples were polished with SiC paper with a grain size of 15, 5, and 1 μm, followed by a polishing cloth containing 1 μm diamond paste. Samples were finished on a table mounted vibrating disk topped with a polishing cloth containing colloidal silica. After polishing, samples were rinsed and sonicated for 10–30 s with DI water and ethanol and dried overnight at 50 °C and coated with 20 nm of gold. In most cases sample imaging by SEM (see below) followed the SIMS analyses and this gold coating was removed by gentle polishing with a 1 μm diamond powder. However, for the SIMS sessions numbered 4.4, 4.5, and 4.6 (see below) samples were analyzed on the SIMS after SEM imaging, and the gold coating was applied after removing the carbon coating used in the SEM.

Over 9 months a total of 146 spot analyses were collected from the suite of proposed analytical standards. All four analytical sessions lasted about 1 week each and these are given separate ‘session’ numbers. Sessions 3 and 4 contained a few sub-sessions numbered after the decimal point as 3.1. For each spot analysis a 13 keV primary beam of $^{16}\text{O}^+$ ions was focused to a 20–40 μm spot on the sample surface. The primary beam current spanned 0.8 to 5.8 nA between sessions but varied by 10% (2 s.d.) within a single sub-session. Each spot was pre-sputtered for 2 min, followed by data collection at the same beam conditions as the pre-sputtering. Positive secondary ion intensities were measured in pulse counting mode on an ETL electron multiplier using a $^{84} \pm 5$ eV energy filter and magnet peak hopping to switch between isotopes. Count rates of $^{42}\text{Ca}^+$ secondary ions generally varied between ~5000 and ~40,000 cps, largely in response to variations in primary
beam current; in general ~7000 cps of secondary ions were detected per nA of primary beam current. Count rates of 24Mg+ secondary ions (~43,000–95,000 cps), 88Sr+ (~30,000–154,000 cps), and 138Ba+ (~200–9300 cps) varied both due to variations in the intensity of the primary beam and differences in concentration between the nine studied samples. A dead time correction was not applied to the data due to the relatively low secondary ion beam intensities. Each analysis was defined to be 20 or 30 cycles long, where each cycle used magnetic peak hopping to rotate through the sequence of detected ions, 24Mg+, 42Ca+, 88Sr+, and 138Ba+, and each species was integrated for 2 or 4, 1 or 2, 1 or 2, or 15 or 30 s per cycle, respectively (numbers of cycles and dwell times per cycle varied from session to session). A few analyses were made with 180 cycles to estimate the effect of acquisition time on measured isotopic compositions.

Because of the chemical complexity of geological materials, molecular interferences can be significant in SIMS analyses. It has been demonstrated that energy filtering reduces interferences from molecular ions during measurements of 24Mg+, 42Ca+, 88Sr+, and 138Ba+ from carbonate materials (Herzog et al., 1973; Shimizu et al., 1978; Allison, 1996; Hart and Cohen, 1996; Demistone et al., 1997; Gaetani and Cohen, 2006). As an additional check for molecular interferences in this study, we performed high mass resolution scans of secondary ions including 24Mg+, 42Ca+, 88Sr+, and 138Ba+ from carbonate materials (Herzog et al., 1973; Shimizu et al., 1978; Allison, 1996; Hart and Cohen, 1996; Demistone et al., 1997; Gaetani and Cohen, 2006). As an additional check for molecular interferences in this study, we performed high mass resolution scans of secondary ions including 24Mg+, 42Ca+, 88Sr+, and 138Ba+ from carbonate materials (Herzog et al., 1973; Shimizu et al., 1978; Allison, 1996; Hart and Cohen, 1996; Demistone et al., 1997; Gaetani and Cohen, 2006). An example of the small peak corresponding to the calcium dimer (44Ca2+) is 0.012 amu from the peak center of 88Sr (Fig. S-1C). Assuming that the center of 44Ca2+ is at 87.917 amu and the peak is symmetrical, the intensity of 44Ca2+ is expected to be negligible at the center of the 88Sr+ peak (87.905). A scan of 88Sr+ using an energy offset of ~20 eV yielded an even smaller 44Ca2+ peak relative to those obtained without energy offset (Fig. S-2). Overall, the 44Ca2+ contribution to 88Sr+ is below 0.3% of measured 88Sr+ intensities at analytical conditions used in this work.

2.4. NanoSIMS

The Caltech Cameca NanoSIMS 50-L was also run in several sessions over 12 months. Unlike most other Cameca IMS machines, the duoplasmatron on the NanoSIMS is vertically oriented and the exit hole of the source becomes obstructed with soot or other particulate matter during operation and many analytical sessions had to be restarted after failure of the 16O− primary beam. As with the 7f-Geo runs, these sub-sessions were numbered after the decimal point as 2.1, 2.2, 2.3, etc.

Where data are collected under significantly different conditions than those described below, we note it in the Results and Discussion sections. The sample preparation procedure was the same as for the ims 7f-GEO samples with the exception that samples were kept in the NanoSIMS vessel chamber for up to a day prior to analysis to evaporate volatiles and reach the required vacuum condition (~10−9 Torr).

When using an 16O− primary beam on the NanoSIMS, intensity and spot size are largely controlled by two apertures. Two Faraday cups (FCp), located at the end of the intermediate section and (FCo) occasionally positioned in place of the sample are used to regularly assess incident primary beam current. Over all our analytical sessions FCp and FCo varied from 195 to 580 nA and 3 and 23 pA respectively. Measurements were performed with an 8 kV primary beam.

We determined the spot size of the primary 0− beam on the sample surface following methods described in Gagnon (2009); i.e., by imaging a sharp compositional boundary and defining the beam width to lie between 16% and 84% of that contrast. Measured beam widths generally varied between ~500 and 800 nm for primary beam currents varying between 0.5 and 5 pA (where most data generated as part of this study was collected using a relatively intense primary beam with a width nearer the upper end of this range). As an undamaged gold coat is required to minimize sample charging, spacing between adjacent analytical spots was generally limited by the width of ‘burn marks’ (regions where the gold coat was discolored), which were generally on the order of 2−3 μm across. For single spot analyses we pre-sputtered for 2 min at the same beam conditions used for analysis in the session #1–3. In analytical session 4 we rastered the beam over a 2 μm × 2 μm area and pre-sputtered for 10 min with a primary beam approximately twice the intensity used for analysis.

Positive secondary ion intensities for all masses were collected simultaneously with Hamamatsu discrete dynode electron multipliers in pulse counting mode. Count rates of 42Ca+ typically varied between ~700 and ~7000 counts per second (cps), depending on the intensity of the primary ion beam. Count rates of 24Mg+ (~2–3700 cps), 88Sr+ (~12,272 cps), and 138Ba+ (~700–7900 cps) varied more widely due to both primary beam current variations and differences in composition among the different standards. For single spot analyses either 200 or 500 total cycles were collected, but for the 2 μm × 2 μm raster of session #4 120 cycles were used. Integration times for each cycle were 3 s in analytical session #4 and 1 s in all other sessions. No dead-time correction was applied to the data.

The NanoSIMS analyses generally had mass resolutions in the range from 1950 to 2810 under the tuning conditions used for this study. Under these conditions, mass scans did not show any molecular interferences at 24Mg+, 42Ca+, and 88Sr+ (Fig. S-1D–F). However, we infer that 86Sr must have suffered from isobaric interferences from the 44Ca2+ dimer, which can only be separated at MRP > 9000 (Weber et al., 2005). We corrected for these inferred interferences by assuming that the Ca dimer formation rate is similar for all carbonate samples and standards examined in this study, and that the 44Ca2+ contribution can be treated as a constant background present in all standards and samples that shifts all measured 88Sr/42Ca ratios higher by a similar absolute offset (see Appendix 2 for more details). We calculate the contribution of 44Ca2+ to the 88Sr+ peak using:

\[
\frac{44Ca_2^+}{88Sr^+} = \frac{[44Ca_2^+]}{[88Sr^+]} = \frac{1.1 \cdot 10^{-3}}{1.1 \cdot 10^{-3}}
\]

where \(42Ca^+\) is the measured \(42Ca^+\) intensity – a known value for every cycle of every measurement. Here \(44Ca_2^+/40Ca^+\) (1.7 \cdot 10−3) is the ratio of the count rates at masses 80 and 40. \(44Ca/40Ca\) (6.5 \cdot 10−3) is the natural abundance ratio, and \(44Ca_2^+/40Ca_2^+\) (4.32 \cdot 10−3) is the ratio of the dimer formation determined by Weber et al. (2005). This correction ratio is identical, within error, to the y-intercept in our Sr/ Ca versus 88Sr+/42Ca+ calibration plots (see below), giving us confidence in this interference correction scheme. Hydrides are another potential source of isobaric interferences, but count rates of all of the potential species (chiefly 137BaH+ and 23NaH+) are too small to affect our reported Me/ Ca ratios.

2.5. Other techniques

We used a variety of standard \(in situ\) solid imaging and analytical techniques to provide context for our \(in situ\) SIMS analyses of the Me/ Ca ratios. Samples were mounted into aluminum cylindrical holders of 1.2 and 2.5 cm in diameter using Araldite epoxy. Each holder contained up to ten different reference calcites and aragonites. All samples were carbon coated.

Backscattered (BE) and secondary electron (SE) images were obtained using a 1550 VP Field Emission SEM at 15 kV, 5–8 nA of current, and a 120 μm aperture. Chemical analyses of major and minor elements were done on an Oxford INCA Energy 300 X-ray Energy Dispersive Spectrometer (EDS) system. More precise chemical analyses of major and minor elements were done by a JEOl JXA-8200 electron microprobe (EMP) at 15 kV and 10 nA current with a spot size of 2–3 μm. Phase identification was performed on a Renishaw M1000 micro-Raman spectrometer and HKL Electron Back Scatter Diffraction (EBSD) system (see Ma and Rossman, 2008 for description of analytical equipment).
3. Results

Separate spot analyses from different parts of each standard crystal, or on the different grains of NBS-19, form the basis of our data set. In all, 123 spots were analyzed by NanoSIMS and 146 spots were analyzed using the 7f-Geo. These data are tabulated in Tables S-1–S-7. Our goal is to understand heterogeneity in the various standards, but we first need to examine how variable the reported intensity ratios are for a single spot. For the 7f-Geo we monitored the effect of acquisition time on the behavior of intensity ratios by performing a few relatively long acquisitions. Fig. 1A–C show results for 60 and 180 cycles of collection, versus our normal 20 cycle method, for $^{88}\text{Sr}/^{42}\text{Ca}$, $^{24}\text{Mg}/^{42}\text{Ca}$, and $^{138}\text{Ba}/^{42}\text{Ca}$ ratios. Here data from OKA, Blue-CC, and NBS-19 are normalized to their mean values and plotted against the number of cycles collected (where all cycles are of a constant duration, 17 s for OKA and 30 s for Blue-CC and NBS-19). Even after pre-sputtering for 2 min, the intensity ratios drift during a single spot analyses. We suggest these patterns arise from the sputtering process, rather than from true compositional

![Graphs showing intensity ratios for different standards](image-url)
variation with depth, because spots at different locations and in different carbonate materials exhibit similar drifts. After the initial period of rapid drift, ratios approach a steady-state with a relatively stable ion-impregnation and sputtering condition that is the ‘sweet spot’ for elemental ratio analysis. The longest run of 180 cycles in NBS-19 also shows relatively high drift in Mg/Ca after about cycle 130, which might reflect deep craters and/or other damage of the sample surface from this long sputtering time.

NanoSIMS primary beam intensities at the sample surface were three orders of magnitude smaller than those of the 7f-Geo so longer acquisition times were required. In one case we extended the number of cycles to 500 as a test of intensity ratio stability (Fig. 1D–F). $^{24}$Mg/$^{42}$Ca ratios on the NanoSIMS drift with increasing cycles collected in a manner very similar to the 7f-Geo data. In contrast, the ratios of $^{88}$Sr/$^{42}$Ca and $^{138}$Ba/$^{42}$Ca from the NanoSIMS analyses do not show steep increases at the start of each analysis but rather drift linearly upward (Fig. 1E,F). However, similar to the SIMS data, the large scatter of the less intense $^{88}$Sr/$^{42}$Ca and $^{138}$Ba/$^{42}$Ca beams in Blue-CC and 135CC may mask the drift of the ratios with time. Extending the number of cycles to 500 did not markedly change the intensity ratio drift. However, elimination of the first 150 cycles from all of our normal 200 cycle single spot analyses improved the internal error by up to the factor of two. The first 40 cycles were removed from the data in session #4 for a similar reason.

We are interested in understanding how the observed variability of an intensity ratio compares to the uncertainty in the mean of that ratio as predicted by Poisson statistics. Many SIMS studies examine this property by plotting intensities and primary ion beam fluence. Here we take an approach developed to examine data from a MC-ICP-MS (John and Adkins, 2010). Fig. 2 shows the standard error of the mean for a population of intensity ratios collected for single spots versus the total number of counts collected over the same time. The x-axis is actually the log of ‘n-effective’, $\log\left(\frac{N_x}{N_x+N_{42}}\right)$ where $N_{42}$ is the total counts of $^{42}$Ca, to account for the fact that both the metal of interest ($N_x$) and the $^{42}$Ca beam can limit the Poisson statistics in some cases. For both the 7f-Geo (Fig. 2A) and the NanoSIMS (Fig. 2B), our single spot data demonstrate consistency with counting statistics by scattering around the theoretical line of slope $-1/2$ (Appendix 3).

To better understand how these statistics evolve during the analysis of a single spot, a continuous error plot of the three intensity ratios from the 180 cycle NBS-19 run on the 7f-Geo is shown in Fig. 3A. Points correspond to successive additions of 10 cycle blocks, starting with cycles 11–20, to the cumulative data set for a given intensity ratio, such that the last point corresponds to the data for cycles 11–180. The effect of a mean shift in the $^{24}$Mg/$^{42}$Ca ratio towards the end of the spot analysis can be seen in the increase in standard error at the end of the series of diamonds in Fig. 3A. In general, spot analyses parallel the counting statistics line after a few tens of cycles, improving our confidence that chopping the first 10 cycles of data is enough to eliminate all but the statistical sources of internal error. As most of the single spots were analyzed for 20 cycles only, each spot analysis in the ims 7F-GEO is shown in Fig. 3A. Points correspond to successive additions of 10 cycle blocks, starting with cycles 11–20, to the cumulative data set for a given intensity ratio, such that the last point corresponds to the data for cycles 11–180. The effect of a mean shift in the $^{24}$Mg/$^{42}$Ca ratio towards the end of the spot analysis can be seen in the increase in standard error at the end of the series of diamonds in Fig. 3A. In general, spot analyses parallel the counting statistics line after a few tens of cycles, improving our confidence that chopping the first 10 cycles of data is enough to eliminate all but the statistical sources of internal error. As most of the single spots were analyzed for 20 cycles only, each spot analysis in the final data represents the average of cycles 11 through 20. Fig. 3B–D shows a similar analysis for the NanoSIMS behavior over the 500 cycle run. Again, data quickly begin following counting statistics and intensity ratios after a few cycles for elements of widely different masses. Overall the 7f-Geo and NanoSIMS data follow Poisson statistics to much better than 1% precision ($2\sigma$) for Me/Ca ratios with long acquisition times and enough total counts.

4. Discussion

4.1. Heterogeneity in solid standards

Any analytical technique that directly measures solid samples is subject to problems of standard inhomogeneity. Our approach to tackling this problem has been to nest measurements of very high spatial resolution from the NanoSIMS in a grid of lower resolution measurements from the SIMS. When these data are combined with backscattered electron (BE) images of the analyzed domains (generated with the SEM), we can evaluate which of the many standards used in the community is truly homogeneous, or at least develop strategies for avoiding heterogeneity.

While the ICP-MS data are our reference frame for the accuracy of the SIMS analyses, they also reveal something about the variability of Me/Ca ratios in the standards themselves. In Fig. 4, standards are ordered from highest to lowest Sr/Ca and Mg/Ca in each column. Data from this study (circles) are compared to literature data (dashed lines; Fig. 4). There is a $>7$% range in Sr/Ca for all standards except UCI, RPI, and HUJ calcites. Similarly, there is a $>7$% range for the Mg/Ca ratio in all standards except UCI calcite. We interpret this variability as evidence for chemical heterogeneity of standards, and suggest it provides a likely explanation for the difference between our data and the literature values.

The ICP-MS data in Fig. 4 demonstrate that there are two types of variability we need to assess: Ratios of Sr/Ca and Mg/Ca are more homogeneous within single crystals of Blue-CC than they are in OKA. However, inter-crystal variation of Blue-CC, especially in Mg/Ca, is large when compared to OKA. These are two of the more commonly used SIMS CaCO$_3$ standards; both are clearly heterogeneous yet they have different styles of heterogeneity—perhaps requiring two different strategies for effective use as calibration standards. All standards examined here with two or more crystals show both Sr/Ca and Mg/Ca ranges
Similar to aragonite or strontianite. For all other standards measured in this paper, the backscattered electron images are relatively homogeneous within an area of \(-1\) mm\(^2\). OKA is the only standard with discrete mineral phases other than CaCO\(_3\).

We used the 7f-Geo to map the spatial variability in several OKA crystals. Here we compare the 88Sr/42Ca and 24Mg/42Ca data from one analytical session to a backscattered BE map from the SEM (Fig. 6). This subset of all our spatially located data was chosen because of all the crystals analyzed it has the largest number of SIMS Me/Ca ratio measurements. All other BSE images of the OKA standard, together with cross plots of the SIMS data, are shown in Figs. S–3–5, and Tables S-1 and S-5, but they contain essentially the same patterns described here. Three types of calcite are evident from the different intensities of the grayscale image of BE intensity. The greatest area of homogeneous ‘matrix’ (light gray) contrasts with dark islands or lines (Fig. 6A). The small inclusions of strontianite and barite shown in Fig. 5 are the brightest spots entirely surrounded by dark regions in Fig. 6A.

Isotopic intensity ratios from the SIMS data show that the matrix is generally enriched in Sr and Ba, but depleted in Mg, relative to the darker SEM regions (Fig. 6B and C). In these scatter plots, the magenta ovals correspond to heterogeneous areas including holes, inclusions, dark islands, dark lines, and areas of variable SEM intensities.

SIMS spot sizes for this analytical session are shown as numbered ovals on the BSE image in Fig. 6A. Clusters of the data in Fig. 6B and C document that the matrix of OKA is an excellent candidate for use as a SIMS standard. 88Sr/42Ca, 24Mg/42Ca, and 138Ba/42Ca data in this region have standard deviations (1 s.d.) of 0.85%, 0.81%, and 1.5% respectively; a variability that is similar to the internal errors of the individual points. The darker, lower intensity regions, on the other hand, are highly variable in their Me/Ca ratios (Fig. 6). There is no easily identifiable pattern in these data, but they are clearly more complex than the compositional variations expected for mixing between two end members (e.g., matrix material mixed with inclusions of fixed composition). Overall, the range of variability from the ims 7f-Geo data set is larger than that for the ICP-MS data. This is expected due to the larger amount of material that must be micro-milled for isotope dilution experiments compared to the spot sizes of the SIMS instrument.

We checked for even higher resolution Me/Ca ratio variation in OKA by measuring ten NanoSIMS spots on OKA-II; a different crystal than shown in Fig. 6. The data in Fig. 7 span a 90 \(\mu\)m long chain with 10 \(\mu\)m separating each spot. Similar to the wide area spatial study with the 7f-Geo, most of the data form a cluster having a mean that is high in 88Sr/42Ca and 138Ba/42Ca, and low in 24Mg/42Ca relative to the three outlying data-points. Though we lack an SEM image for the analyzed area, the data suggest that this NanoSIMS profile crossed a heterogeneous, BSE-dark calcite zone. We speculate that spot #3 (with the lowest 88Sr/42Ca and 138Ba/42Ca and the highest 24Mg/42Ca) was in the center of a BSE-dark zone and that spots 2 and 4 were at the sides (Table S-5).

It is not possible to directly compare data generated with the 7f-Geo and the NanoSIMS for any one type of carbonate in the OKA sample (i.e., BSE dark vs. light) using conventional standardization schemes because it is obvious from Fig. 4 that this material is compromised by inter and intra-grain heterogeneities. However, if we assume that each fabric (e.g., the ‘matrix’ in BSE images) is uniform within and between grains, we can normalize data generated on these two machines using the following equation:

\[
\frac{88\text{Sr}}{42\text{Ca}} \text{Nano-SIMS}\nonumber
\]

\[
= \frac{88\text{Sr}}{42\text{Ca}} \text{Nano-SIMS} \frac{7f\text{-ims average}}{\text{matrix}} \nonumber
\]

\[
= \frac{88\text{Sr}}{42\text{Ca}} \text{Nano-SIMS} \frac{7f\text{-ims average}}{\text{matrix}} \nonumber
\]

\[
\text{matrix} = \frac{88\text{Sr}}{42\text{Ca}} \text{Nano-SIMS} \frac{7f\text{-ims average}}{\text{matrix}} \nonumber
\]

The ratios of 24Mg/42Ca and 138Ba/42Ca were adjusted in the same way. The scale of variability seen in the 7f-Geo data set is about 2 \(\times\) that seen in the NanoSIMS data despite a \(-100\times\) increase in the area sampled. This implies that textures seen in the SEM images seem to be a good
guide for the spatial variability in OKA, and that the ‘matrix’ of this standard is homogeneous at essentially the level we can measure it.

Three other potential SIMS standards all have smaller overall Me/Ca ratio ranges compared to the bulk OKA data, but none of them are as homogeneous as the matrix portion of OKA (Fig. 8 and Table S-2). Thus, paradoxically, the best standard available to the community may be one of the fabrics in this complexly zoned material. In Blue-CC, the standard deviation (1 s) of $^{88}\text{Sr} / ^{42}\text{Ca}$, $^{138}\text{Mg} / ^{42}\text{Ca}$, and $^{138}\text{Ba} / ^{42}\text{Ca}$ ratios are 2.37%, 1.60%, and 4.91% respectively across eight data-points. We find that $^{88}\text{Sr} / ^{42}\text{Ca}$ ratios measured by SIMS vary more widely than Sr/Ca ratios determined for single crystals by ICP-MS, suggesting that heterogeneity in Sr/Ca increases at smaller scales in Blue-CC. NBS-19 has slightly larger heterogeneity in $^{88}\text{Sr} / ^{42}\text{Ca}$ and $^{24}\text{Mg} / ^{42}\text{Ca}$, with standard deviations <5% in both ratios, but $^{138}\text{Ba} / ^{42}\text{Ca}$ in NBS-19 is up to a factor of three more variable than in Blue-CC. While these ranges in Me/Ca ratio may seem acceptable, we have demonstrated that internal errors for single spot analyses are more precise than this spatial variability. NanoSIMS data from Blue-CC shows similar results as those from the SIMS (Fig. 9, Table S-5). While Blue-CC Sr/Ca and Mg/Ca ratios span a larger range than the matrix portion of OKA, this standard is overall more homogeneous than OKA. It is clear that the ‘matrix’ portion of OKA is the best candidate for a community wide SIMS standard, but it is important that each lab document where standardization spots come from relative to the other inhomogenieties in OKA. In addition we suggest that standardization based on analyses of all of these materials is only accurate if one has independently determined Me/Ca ratios of the

Fig. 4. ICP-MS data from seven standards and across single and multiple crystals. Dashed lines correspond to data obtained from the literature or from personal communications. OKA: Gaetani and Cohen, 2006; Blue-CC: Anne Cohen (personal communication); 135CC: Kent Ross (personal communication) specimen from Harvard Mineralogical museum (#97189) Oberdorf, Austria; LAS-20 and NBS-19: Sano et al. (2005); RPI: Cherniak (1997).
particular crystal used as a standard. There can be wide variability in absolute Me/Ca ratios between different crystals of the same nominal standard.

4.2. Comparing ratios across separate analytical sessions

While it is possible to characterize the variance of a single standard by examining data from within a single analytical session, we also wish to calibrate a standard’s Me/Ca ratio accurately over a long time, spanning many analytical sessions. For our data set we can use the matrix portion of OKA to standardize the intensity ratios of Blue-CC crystals within a single analytical session, and then compare these values across multiple sessions. We choose these two standards for our analysis because they are homogeneous at nearly the level of our internal precision. Fig. 10 and Table S-3 show 7f-Geo Sr/Ca, Mg/Ca, and Ba/Ca values for a single crystal of Blue-CC standardized to the matrix portion of OKA across several analytical sessions, some with multiple sub-sessions. The horizontal lines are our ICP-MS determined values for Sr/Ca and Mg/Ca in this Blue-CC crystal. In general, when collected and standardized carefully, Me/Ca ratios from the 7f-Geo are precise and reproducible, following the level of their internal statistics to better than 1% (2 s), across many months of running the machine. We find scatter during individual sub-sessions that is larger than our internal error, but we attribute this to the slight heterogeneity of Blue-CC itself. The 7f-Geo follows Poisson statistics for each spot, and these spots can be

![Fig. 4 (continued).](image-url)
normalized to each other over long time periods by running the matrix portion of OKA during all analytical sub-sessions where the duo-plasmatron is on continuously.

Using this same approach to normalize intensity ratios across runs with the NanoSIMS gives Blue-CC ratios with much larger scatter. Fig. 11 shows the run-to-run variability for the NanoSIMS data but now with two Blue-CC crystals shown separately because of their large difference in absolute Mg/Ca ratio (Table S-6). We also show the effect of normalizing to either the matrix region in OKA or to the granular NBS-19 standard. The results are much worse than for the 7f-Geo.

In many cases the variability within an analytical session is larger than the differences between sessions, indicating that our normalization works to the degree that a Blue-CC crystal is actually homogeneous. However there is evidence that Mg/Ca and Sr/Ca data are normalized differently in different analytical sessions. For Blue-CC-II in session 2 the Mg/Ca and Sr/Ca data are similarly offset from the accurate value in all sub-sessions. This is not true for Blue-CC-IV where some sub-sessions have Sr/Ca data that fall within the calibrated value and Mg/Ca data that does not. Then other sub-sessions have Mg/Ca data that seems accurate while the Sr/Ca is not.

There is an important difference in the ion optics of the NanoSIMS-50L and the 7f-Geo that could account for these results. The distance between the extraction lens and the sample surface in the NanoSIMS-50L is shorter than in the 7f-Geo by a factor of ~13 (300–400 μm against a 4.7 mm). Small differences in the incidence angle and energy of the primary beam affect the emission cone of the secondary ions, which can lead to substantial element-to-element fractionations in the secondary beam, such that moving the sample holder from sample to standard can result in a different mass bias for the same elemental ratio in the NanoSIMS where the extraction optics are very close to the sample surface. In this case, the relative precision of an intensity ratio within a single sample is governed by the internal error, but the overall accuracy can be as bad as ~7.5% for Sr/Ca and ~11.0% for Mg/Ca. We did not observe systematic variations in instrumental mass fractionation with

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**Fig. 6.** Large spatial analyses of OKA using the SEM and ims 7F-GEO SIMS. (A) SEM BE image of the lower right part in the OKA-II. Numbered spots are from ims 7F-GEO session 4.5. (B, C) Plots of \(^{88}\text{Sr} / ^{42}\text{Ca}\) versus \(^{138}\text{Ba} / ^{42}\text{Ca}\) and \(^{88}\text{Sr} / ^{42}\text{Ca}\) versus \(^{24}\text{Mg} / ^{42}\text{Ca}\) from OKA-II (ims 7F-GEO, session 4.5). The ovals on SEM image correspond to the location and approximate size of the beam burn marks. The blue diamonds are the data collected from the homogeneous calcite matrix. The magenta rectangles correspond to heterogeneous areas including holes, inclusions, dark islands, dark lines, and areas of variable intensities (e.g.: spot no. 12). The error bars are 2σ. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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**Fig. 7.** Elemental variability in OKA-II using the NanoSIMS-50L. A) \(^{88}\text{Sr} / ^{42}\text{Ca}\) versus \(^{138}\text{Ba} / ^{42}\text{Ca}\) and B) \(^{88}\text{Sr} / ^{42}\text{Ca}\) versus \(^{24}\text{Mg} / ^{42}\text{Ca}\) intensity ratios. Also shown are all the ims 7F-GEO data from sessions 3.8, 4.4, 4.5, and 4.6. NanoSIMS-50L data from a 90 μm long line of spots (session 2.1) were normalized to ims 7F-GEO OKA-II matrix data from session 3.8 using Eq. (1) in the text. 2σ error bars of ims 7F-GEO data appear in Fig. 5.
with respect to changes in either the primary or secondary lens settings and thus favor the sample holder geometry relative to the beams as the most likely explanation for worse run-to-run precision on the NanoSIMS compared to the 7f-Geo.

Comparing the accuracy of many standards, not just the most homogeneous ones, across several analytical sessions also shows differences between the 7f-Geo and the NanoSIMS. Fig. 12 shows 7f-Geo intensity ratios plotted against elemental ratios from our ICP-MS measurements for the same standard. Regardless of the day they were run, linear fits over nearly 2 orders of magnitude in Me/Ca ratio show very similar slopes (Table S-4). For the 7f-Geo our data shows it is possible to use single carbonate standards of very different Sr/Ca and Mg/Ca ratios to normalize unknown samples with only a slight increase in uncertainty over the propagated internal measurement statistics. Unfortunately this same plot is not as consistent for the NanoSIMS (Fig. 13, Table S-7).

Within a single sub-session, where all the standards were in the same sample holder, the linear fits across three or more standards are also quite good. Across at least one order of magnitude of concentration, intensity matching of carbonate samples and standards does not seem to be necessary on the NanoSIMS. However, between analytical sessions large changes occur in the calibration slope. We have noticed that these changes are associated with the different extents of pre-sputtering between sub-sessions, the probe current, and the spot size. The probe current at the sample holder was not recorded routinely, but a few values show that an increase from 3.5 pA (session 4.2) to 23 pA (session 4.1) was associated with an increase in the Sr/Ca slope from 0.06752 to 0.11935 and a decrease in the Mg/Ca slope from 0.05279 to 0.02609. This is probably another manifestation of the NanoSIMS ion optics where slight differences in the positioning of the primary beam and the extraction lens can lead to large elemental fractionations.

5. Conclusions

We find that making accurate and precise Me/Ca ratio measurements in carbonate materials on both SIMS machines requires some important attention to the details. Due to inter and intra crystal variability, each crystal used as a standard must be separately and independently characterized for its bulk Me/Ca ratio to at least confirm literature values. This is especially true for Blue-CC where separate crystals can have large differences in their elemental concentrations. In general, intensity matching of standards to sample Me/Ca ratios is not as important as finding homogeneous materials for calibration at reported Me/Ca range.

Both SIMS machines demonstrate internal variability that are dominated by counting statistics to better than 1% precision. However, only certain standards are homogeneous enough within individual crystals to be useful precision and accuracy monitors. Despite the heterogeneity of bulk OKA, its matrix calcite is the most homogeneous material examined in this study (and the best widely available standard). Ims 7F-GEO and NanoSIMS-50L analyses show that external 2σ variations are <0.5%

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Fig. 8. Plots of $^{88}\text{Sr}/^{42}\text{Ca}$ versus $^{138}\text{Ba}/^{42}\text{Ca}$ and $^{88}\text{Sr}/^{42}\text{Ca}$ versus $^{24}\text{Mg}/^{42}\text{Ca}$ from Blue-CC-II (A, B), NBS-19 (C, D), and 135CC (E, F). Data were obtained during ims 7F-GEO session 3.8.
for Sr/Ca and Mg/Ca, and < 1% for Ba/Ca. In our study Blue-CC and AG-1 are the second most homogeneous materials in Sr/Ca (2σ < 2%), and Blue-CC is the second most homogeneous material in both Mg/Ca (2σ < 2%) and Ba/Ca (2σ < 4%). UCI calcite is homogeneous within a single crystal.

There are discrepancies between our bulk analyses and those reported in literature. Therefore, adjacent pieces (within a few mm distance) of each studied SIMS or NanoSIMS standard must be analyzed independently with conventional methods. Independent measurements are required for most of the standards even if they are from the same batch. The possible exception is the OKA standard where Me/Ca inter-crystal variability could be caused by a different distribution of inclusions of barite, strontianite, and heterogeneous (dark) calcite. Our ID-ICP-MS Mg/Ca data for NBS-19 are different from those published by Sano et al. (2005) by 17%, suggesting that Mg/Ca varies between different batches of NBS-19.

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Appendix 1. Description of the standard materials

OKA calcite (OKA-C), Blue-CC calcite (#0875), and AG-1 (aragonite) were provided by Anne Cohen and Glenn Gaetani (WHOI). OKA-C is from the OKA carbonatite complex in Quebec, Canada. AG-1 is a small single aragonite crystal from Spain purchased from Alfa Aesar; note that trace and minor element compositions in other crystals from the same batch are unknown. NBS-19 (in literature also referred to as TS-Limestone) was obtained from a single slab of white marble, provided by the US National Bureau of Standards (Friedman et al., 1982). The 135-CC specimen (Iceland Spar) from the Harvard Mineralogical Museum (#97189) was collected in Oberdorf, Austria and was provided by Kent Ross at UC-Berkeley. LAS-20 is a U-rich calcite from a speleothem in the Vinschgau Valley of northern Italy (Spotl et al., 2002), provided by Neil Sturchio (UL-Chicago). RPI-CC is another Iceland Spar calcite from Mexico, provided by Daniele Cherniak (the mineral dealer was Northeast Geological Supply). HUJ-AR is an aragonite provided by Jonathan Erez at the Hebrew University in Jerusalem and UCI-CC is a calcite provided by Ellen Druffel at UC-Irvine.

Appendix 2. Interferences in NanoSIMS

Unlike the ICP-MS, doubly-charged species are not typically detected on the NanoSIMS reflecting the different energies and physics for ion formation between these methods. However, molecular ions are present in the secondary ion beam, and can interfere with the species of interest. To this end the adjustment of the sample voltage was investigated as a tool to reduce molecular isobaric interferences, but as the sample voltage offset becomes more negative, there is a disproportionate penalty in sensitivity (Fig. S-6) and under the analytical conditions used for this set of experiments it is not a useful approach. But an offset of about \(-15\) V to \(-25\) V, corresponding to a wide and stable maximum in secondary beam current, is still necessary to ensure good sensitivity and stability to accommodate steady-state charge build-up on the insulating \(\text{CaCO}_3\) samples. Since molecular species cannot be
eliminated, interferences from these species must either be resolved using the high mass resolving power of the NanoSIMS-50L or corrected of interference by monitoring molecular formation.

Appendix 2.1. Dimer interferences

Two approaches to correcting for dimer interferences are possible.

(1) Following Weber et al. (2005), the relatively clean and resolvable calcium dimer peak at mass 80 can be used to monitor dimer intensity. Assuming natural abundances for the calcium isotopes, the dimer contribution can then be subtracted off-line from mass 88 using the \(^{44}\text{Ca}\) intensity and the 80/40 ratio. For an accurate correction, this approach assumes either a similar gain in the detectors measuring dimer ratio and mass 88, or a known electron multiplier gain ratio between detectors. We did not routinely monitor detector gain during the analytical sessions presented in this paper. However, in one session, a steady \(^{40}\text{Ca}^+\) beam that was centered into each of the seven EMs resulted in a signal that varied from 10^5 cps to 1.5 \times 10^5 cps across the detectors. Under these conditions explicit corrections are not accurate, but can still be used to roughly estimate the impact of dimer interference on uncorrected Sr/Ca ratios. The dimer formation rate \((^{40}\text{Ca}^2+^{40}\text{Ca}^+\) ratio) was monitored in two of our NanoSIMS analytical sessions (4.1 and 4.2). In session 4.2 \(^{40}\text{Ca}^2+^{40}\text{Ca}^+\) was 1.7 \pm 0.2 \times 10^{-3} for all the standards except OKA and LAS, which both exhibit a lower dimer yield of 1.5 \pm 0.2 \times 10^{-3}. There was no trend in dimer formation rate with time. To establish the importance of dimmers, we assume similar gains...
between the mass 80 and mass 88 detectors; calcium dimers are expected to account for only 1% to 2% of the measured 88 signal for the high Sr/Ca standards OKA and HUJ, 3% to 8% for most of the remaining standards, and ~50% for the low Sr/Ca standard RPI.

(2) In this alternative approach, 44Ca2 contribution to 88Sr can be treated as a constant background in all standards and samples that shifts all measured 88Sr/42Ca ratios higher by a similar absolute offset. This dimer background contribution is then operationally accounted for by the intercept in a linear calibration curve. While dimer yield is similar for most materials, both OKA and LAS exhibit an ~15% lower 44Ca2/42Ca+ ratio (see above). For OKA the dimer is already only a very minor correction, 15% of 1‰ is insignificant, and for LAS the error in the dimer correction is <2‰. These effects are small so we treat the dimmer interference as a background correction during data analysis.

We can roughly estimate the intercept of the Sr/Ca ICP-MS vs. 88Sr/42Ca NanoSIMS calibration curve, assuming no other interferences and perfect ICP-MS accuracy. In session 4.2, 44Ca2/42Ca+ is roughly 1.7 · 10−3, and 44Ca2/42Ca is 6.5 · 10−3 consistently through the run. Assuming natural abundances, the contribution of calcium dimer at mass 88 is 4.32 · 10−3 times the 44Ca2 counts (Weber et al., 2005). Now assuming similar gains in all the detectors, the estimated y-intercept of the calibration curve should be: (1.7 · 10−3)/(6.5 · 10−3) · (4.32 · 10−3) = 1.1 · 10−3, which is within the range of the measured y-intercept of 0.8−2.2 · 10−3. Only one Sr/Ca calibration line has a slightly negative intercept of −7.6 · 10−5 (session 3.1). This analysis shows that dimers are present, that they need to be accounted for, and that they can be corrected for during routine multi-standard calibrations as long as samples and standards are all CaCO3 with only minor impurities and exhibit no dimer formation matrix effect (i.e., differences among samples and/or standards in the relative proportions of dimers).

Appendix 2.2. Hydride interferences

Strontium hydride formation was also estimated from 87SrH+ to 88SrH+ in a strontianite sample, with a similar formation rate of 0.5 to 1%. Typical MRPs for this study were 2000–3000. It should be noted that this definition of MRP includes the flat top part of a peak, corresponding to the exit slit width, and therefore underestimates the ability to optically resolve different masses. The peak edge MRP definition is a more relevant minimum criterion for resolution as it represents the ability to separately measure plateaus on the shoulder of composite peaks. The peak edge MRP, which somewhat overestimates the practical resolving power due to mass stability limitations is typically ~10,000 in this study (5%–95%). Fig. S-1D is a scan of mass 24 during routine conditions demonstrating the resolution of 24Mg+ from the expected location of 2NaH+. While 87SrH+ is a non-resolvable interference on 88Sr+, this interference has little impact on 88Sr/42Ca ratios (<1‰, assuming a hydride formation rate of ≤1%), as 88Sr abundance is much larger than 87Sr. Furthermore, most natural materials exhibit similar 87/88 ratios (within 1%), thus any hydride contribution will scale with Sr concentration, affecting the slope of a calibration curve in a minor way but not impacting the final accuracy.

Appendix 3. Counting statistics in SIMS

According to counting statistics:

$$\frac{\sigma(N_x)}{N_x} = \sqrt{\frac{N_x}{N_x}} \frac{\sigma(N_{42})}{N_{42}}$$

$$\left[\frac{\sigma(N_{42})}{N_{42}}\right]^2 = \frac{\sigma(N_x)}{N_x}^2 \left[\frac{\sigma(N_{42})}{N_{42}}\right]^2.$$  \hspace{1cm} (3.1)

The logarithm of the combined expressions 1.1 and 1.2 yields the following equation for 2σ/mean:

$$\log \left[\frac{2\sigma(N_{42})}{N_{42}}\right] = \frac{1}{2} \log \left[\frac{N_x + N_{42}}{N_x - N_{42}}\right] \pm \frac{1}{2} \log \left[\frac{N_x}{N_{42}}\right].$$

or

$$\log \left[\frac{2\sigma(N_{42})}{N_{42}}\right] = -0.30103 \cdot \frac{1}{2} \log \left[\frac{N_x - N_{42}}{N_x + N_{42}}\right].$$

In Figs. 2 and 3 the logarithms of 2σ/mean are plotted against log (N_x/N_{42}). The logarithms of 2σ/mean was calculated as:

$$\log \left[\frac{2\sigma(N_{42})}{N_{42}}\right] = 2 \cdot \frac{1}{2} \frac{1}{n} \frac{1}{\text{sd}(X/42)} = \frac{1}{n} \frac{1}{\text{sd}(X/42)} \frac{1}{\text{sd}(X/42)}.$$

Here 1 s.d.(X/42) is the standard deviation of 24Mg/42Ca, 88Sr/42Ca, or 138Ba/42Ca ratios between (n − 10) cycles.

Appendix 4. Calculation of Me/Ca ratios from SIMS data

Elemental ratios of Sr/Ca in Blue-CC-III presented in Figs. 10 and 11 were calculated using OKA standard analyzed together with Blue-CC at each sub-session:

$$\frac{\text{Sr/ICP-MS}}{\text{Ca/ICP-MS}} = \frac{\text{Sr/42Ca}}{\text{Ca/42Ca}} = \frac{\text{Sr/42Ca}}{\text{Ca/42Ca}}.$$ (4.1)

The fraction on the left side of the Eq. (4.1) is the Sr/Ca in Blue-CC-III (shown as data-point in Figs. 10 and 11) at the particular sub-session k. The first fraction on the right side of the Eq. (4.1) is the SIMS ratio of 88Sr/42Ca of Blue-CC-III to 88Sr/42Ca of OKA-III obtained at the same sub-session k. The second fraction is the MRP of 88Sr/42Ca of OKA-III to 88Sr/42Ca of OKA-I obtained at session 4 (when both OKA-III and OKA-I were analyzed with 75F-GEO). The ratio of Mg/Ca in Blue-CC-III were obtained in the similar way. For Ba/Ca ratio in OKA the literature value of 1.61 mmol/mol was used (see Gaetani and Cohen, 2006). The true Sr/Ca ratios were determined by normalization of the SIMS data from Blue-CC-III to those from Blue-CC-I:

$$\frac{\text{Sr/ICP-MS}}{\text{Ca/ICP-MS}} = \frac{\text{Sr/42Ca}}{\text{Ca/42Ca}} = \frac{\text{Sr/42Ca}}{\text{Ca/42Ca}}.$$ (4.2)

The ratios of Mg/Ca were determined similarly to Sr/Ca. Please note that the piece broken off Blue-CC-I for SIMS analyses and those dissolved for ICP-MS analyses came from the same single crystal of Blue-CC and were located next to each other. The same is true for all other
Appendix 5. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2013.07.019.

References


